Photoluminescence from White Reference Materials for Spectral Diffuse Reflectance upon Exposure to the Radiation Shorter than 400 nm

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Abstract. Photoluminescent properties of white reference materials used as spectral diffuse reflectance standards were studied in the near UV to visible region. Spectroscopic analysis based on a two-monochromator method revealed that most of white reference materials produced the photoluminescence upon exposure not only to the near UV and UV radiation but also to the visible radiation shorter than 400 nm.

Introduction

Spectral diffuse reflectance measurements in the visible region are quite important for accurate reflectance colorimetry. At the National Metrology Institute of Japan (NMIJ), a national standard of spectral diffuse reflectance in the visible region have been successfully established with the combination of a new integrating sphere-based absolute reflectance measurement, modified Sharp-Little method[1)], and a specially designed integrating sphere with uniform reflectance[2)]. In addition, a new reference spectrophotometer has also been developed and new calibration services directly traceable to the national standard is now in operation[3)].

General way to calibrate the spectral diffuse reflectance is substitution or comparison measurements. In principle, spectral diffuse reflectance of samples, in many cases white diffusing materials, can be calibrated by relative comparison to white reference materials of known reflectance. There are strict requirements for the white reference materials in terms of reflection properties, such as short-term and long-term stability, reflectance uniformity, lambertian approximation, non-photoluminescent property, spectral non-selectiveness and so on. At present, some kinds of white reference materials are commercially available, and their reflection properties have been thoroughly investigated and reviewed[4)]. Photoluminescence is one of the most significant error factors related to the reflection properties of the white reference materials to be considered in diffuse reflectance measurements in the visible region, especially in the measurements using commercial instruments based on polychromators. It is well known that most materials produce photoluminescence upon exposure to intense UV radiation, which tends to be more noticeable in the shorter wavelength range. UV-cut filters are usually applied in commercial instruments to eliminate the UV radiation that would cause the photoluminescence from samples. As most white reference materials are considered not to produce photoluminescence upon exposure to the near UV and visible radiation, almost no attention has been paid so far to such kind of photoluminescence except for a few studies that referred to the existence of the photoluminescence on a kind of opal glasses[5)] and ceramic tiles[6)].

However, a series of our research revealed that some kinds of white reference materials produced the photoluminescence even on exposure to the shorter edge part of the visible radiation.

This paper describes the results on the evaluation of the photoluminescent properties for various kinds of white reference materials in the near UV to visible region. The effect of the photoluminescence in the general reflectance calibration is also discussed.

Samples and experimental setup

The photoluminescent properties were studied for these materials; 1) two kinds of pressed and sintered polytetra-fluorethylene (PTFE) resins, 2) two types of matte ceramic tiles, 3) three kinds of matte opal glasses, and 4) three kinds of barium sulfates. These materials are well known for their excellent reflection properties and have been widely used as reflectance standards worldwide for many years.

Spectroscopic analyses in terms of photoluminescence spectra were applied to evaluate the photoluminescent properties of the samples. The photoluminescence spectra were measured with the NMIJ spectrofluorimeter based on the two-monochromator method over the wavelength range from 300nm to 700nm. The wavelength of the radiation for excitation was selected from 300 nm to 450 nm. A commercial spectrofluorimeter (Hitachi, F4500 ®) was also employed to check the reproducibility of the measurements.

The schematic diagram of the optical system of the NMIJ spectrofluorimeter is shown in Fig.1. It consists of two monochromators, a 150W Xe-arc lamp, a photo-multiplier tube (PMT) and some optical components. The first monochromator generates monochromatic radiation with the bandwidth of about 5nm, and the second one monochromatically detects the photoluminescence produced from samples. Relative spectral responsivity of each monochromator was calibrated using a spectral irradiance standard lamp and a Si photodiode with spectral responsivity scale. In this study, some UV-filters and sharp-cut filters were selected according to the excitation wavelength and put in front of the second monochromator to eliminate the reflected radiation.

Results and Discussion

Fig.2 shows a part of photoluminescence spectra of white reference materials; a PTFE resin, two matte ceramic

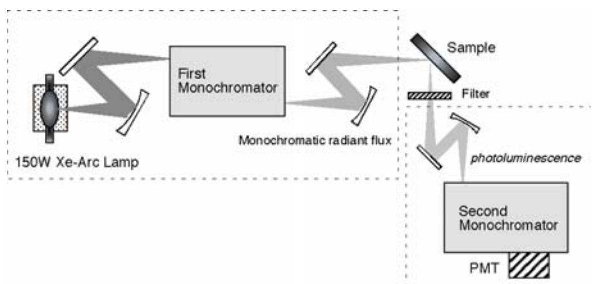

Figure 1. Schematic diagram of the optical system of the NMIJ spectrofluorimeter used in this study.

tiles, a matte opal glass and a sprayed barium sulfate plate, measured in this study. In Fig.2, the excitation wavelength is at 330 nm and 360 nm, respectively.

The matte ceramic tile (1) shows the greenish photoluminescence that has the spectrum with its peak around 530 nm. The matte ceramic tile (2) shows the unique red photoluminescence whose spectrum has relatively sharp structure around 670 nm. The matte opal glass shows the bright blue photoluminescence with the peak around 440 nm. The PTFE resin and the sprayed barium sulfate plate show the weak dark-purple or dark-blue photoluminescence with the peak around 405 nm and 420 nm, respectively. Roughly, the shorter the wavelength for the excitation becomes from 400 nm down to 300 nm, the larger the intensity of photoluminescence from each sample becomes.

From these measurements, it was found that most samples examined in this study showed the photoluminescence not only by the UV radiation but also by visible radiation. It is noticeable results that the photoluminescence was observed from most samples with excitation by the shorter edge part of visible radiation, which has not been considered in diffuse reflectance measurements. Among the five samples shown in Fig.2, the matte opal glass and matte ceramic tiles showed the relatively strong photoluminescence at both excitation wavelengths, whereas the other samples showed weak photoluminescence. The opal glass showed in Fig.2 is the same type of opal glass that the strong photoluminescence due to UV radiation was reported in the past[5]. By contrast,

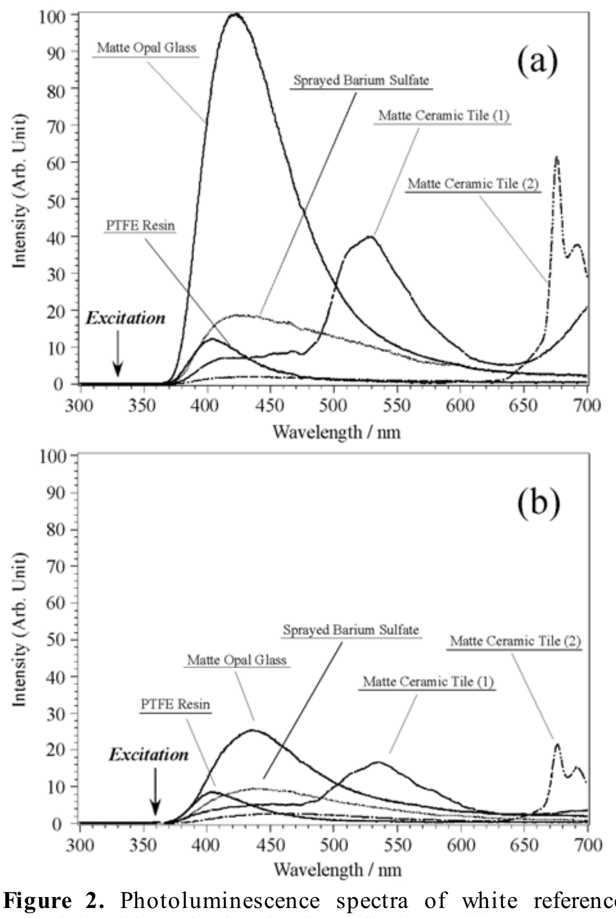

Figure 2. Photoluminescence spectra of white reference materials with excitation by the radiation at (a) 330 nm and (b) 360 nm, respectively. The vertical axis shows the relative photoluminescent intensity from each sample that was normalized using the strongest photoluminescent as unity.

another opal glasses examined in this study showed quite weak photoluminescence upon exposure to the visible radiation, although the spectra are not shown in this paper. Furthermore, photoluminescent properties of PTFE resins and barium sulfate plates showed strong dependence on the purchase date, brand of raw materials, frequency in use, forming procedures and store conditions. It is a tentative result but in this study, appropriately stored or fresh samples of these showed almost no photoluminescence upon exposure to both near-UV and visible radiation. More detailed investigation about the photoluminescent properties of white reference materials including the origin of the photoluminescence is now in progress.

Commercial instruments for spectral diffuse reflectance measurements basically are not equipped with structures to eliminate errors due to the photoluminescence upon exposure to the visible radiation. However, it would cause relatively large error in the spectral diffuse reflectance measurement, depending on the measurement condition such as the spectral responsivity of detectors, bandwidth, spectral distribution of incident radiation, measurement geometry and so on. More thorough attention to the photoluminescence from white reference materials is essential to ensure the accurate and reliable calibration for the spectral diffuse reflectance.

Conclusion

Most of white reference materials used as diffuse reflectance standards tend to produce the photoluminescence upon exposure not only by the UV radiation but also by visible radiation. Such photoluminescent effect was observed at the radiation shorter than 400 nm in this study. Although almost no attention has been paid to such photoluminescence, especially to that due to the visible radiation, it would cause relatively large error in the spectral diffuse reflectance measurement, depending on the various measurement conditions.

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